Crystal Structure of Polyvinyl Alcohol

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were more evidently emphasised by observing photometer curves.

From the above mentioned results, we were obliged to recognize that the aging process in semi-molten poval-filaments was not a crystal growth as in ordinary low molecular substances, but a change of state to approach regular crystalline structure from non-crystalline structure.

71. Aging Phenomena in Poval-filaments.

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Aging phenomena in semi-molten poval-filaments were persued by means of change of its ability of swelling and tolerance to hot water, etc. The swelling degree was represented in percentage of total weight by measuring the maximum water absorption at 30°C. and the ability of tolerance to hot water was measured by softening temperature of filaments hanged in water with constant load and constant temperature elevation. The experiments performed were as follows, (1) Time dependency upon swelling and softening temperature. (2) Effect of temperature, elongation and water contents upon aging. (3) Dilatometric measurement. It was found that there exists a linear relationship between swelling and softening temperature and the temperature facter was more pronounced than other effects. In addition to these facts, some volume contraction (57% P. V. A. 10 days. V. C. 0.256%) during aging were observed.

A relation between velocity of aging and heat-treatment were proposed as follows from theoretical point of view.

$V = AT^{\frac{1}{2}} e^{-E/RT}$, where V=velocity, T=abs. temperature,

E=activation energy.

From the experiments of swelling, it was deduced that the activation energy was 20–30 kcal/mol.

We are now discussing on the numeral deviation from the former report (A. E. 10–12 kcal/mol.), however, anyway it was proved that aging process should take place in the semi-molten poval-filaments.

72. Crystal Structure of Polyvinyl Alcohol.

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It has been said[1] that the molecular repeat distance of polyvinyl alcohol 2.52 Å

indicated not only that the chain had a plane zigzag configuration, but also that all the hydroxyl groups Lay on the same side of the zigzag plane. However, it has been shown recently by C. W. Bunn[2] that the observed repeat distance might be equally compatible with a molecular structure in which hydroxyl groups were randomly placed in left-and right-hand positions because hydroxyl groups might replace hydrogen atoms at random on a carbon chain without destroying crystallinity.

For the explanation of X-ray diffraction of polyvinyl alcohol it is not necessary to assume such a stereochemical irregularity of this molecule[3]. A particular, irregular arrangement of molecules with hydroxyl groups regularly (alternatively) placed in left-and right hand positions accounts in a satisfactory way for the diffraction pattern. It is only necessary to assume that the second molecular chain in a unit cell is displaced from the first 1.26 Å (a length of a carbon atom in the zigzag chain) in the direction of fiber axis randomly up- and down-wards. It can be easily seen that the both displacements may equally likely occur. Although atomic positions given by Bunn fit also for this arrangement, the following parameters give somewhat better agreement with the observed intensities: C (of CH_2) at 0.243 a, 0.250 b, 0.065 c, C (of CH) at 0.293 a, 0.750 b, 0.217 c half of the oxygen atom at 0.166 a, 0.750 b, 0.420 c and the other half at 0.466 a, 0.750 b, 0.480 c. Dimensions of the unit cell are a=7.83 Å, b=2.52 Å, c=5.53 Å $\beta=87^0$.

1) R. C. L. Mooney, J. Amer. Chem. Soc., **63**, 2828 (1941).
2) C. W. Bunn, Nature **161**, 102 (1948).
3) C. W. Bunn, Nature **159**, 161 (1947).

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73. Studies on the Correlation between Chemical Constitution and Insectidal Activity of Halogenated Aromatic Compounds. (V)

Studies on the Chlorinated Compounds of BHC.

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When chlorine gas was introduced into carbon tetrachloride solution of pure γ-BHC under the direct sunlight, γ-BHC was chlorinated very easily. In our experiments, greater part of γ-BHC was chlorinated by 30 minutes reaction at 40°C and unreacted γ-BHC was not detected after 4.5 hours reaction (Reaction A). The reaction products were very viscous oil and fractionated under vacuum. From the results of elemental analysis and polarographic observation, these products were found chiefly to be the mixtures of hepta- and octa-chlorocyclohexanes. On the other hand, isomers of hepta-and octa-chlorocyclohexanes were synthesized purely